

## DESCRIPTION

POLYOLEFIN-BASED RESIN COMPOSITION AND USE THEREOF5 TECHNICAL FIELD

The present invention relates to a polyolefin-based resin composition. The polyolefin-based resin composition of the present invention is flexible, yet exhibits heat resistance, mechanical properties, and solvent resistance 10 in a well-balanced manner, and is thus suitable for use in wire coatings, coatings of various cables, tubes, films, sheets, and various other applications.

BACKGROUND ART

15 Polyolefin-based resins generally show moderate heat resistance and high solvent resistance. This feature makes the compounds suitable for use in a wide range of applications, including wire coatings; cable coatings; tubes; films, such as laminate films, agricultural films, 20 stretch wrapping films, adhesive films, and medical films; sheets, such as agricultural sheets; processed paper; injection molding; pipes; bundling tapes; flat yarns; and fibers. Nonetheless, as far as such applications as wire coatings, tubes, films, and sheets are concerned, further 25 improvements are required in certain physical properties of polyolefin-based resins, including heat resistance and

solvent resistance.

The following several methods or techniques have been proposed in an effort to impart required mechanical properties, heat resistance and solvent resistance to the 5 polyolefin-based resins. In a method <1>, a crosslinkable polymer composition composed of a polyolefin-based resin and a crosslinkable monomer is exposed to an active energy ray (Japanese Patent Laid-Open Publication No. Hei 10-147671). In another method <2>, polyethylene is blended 10 with an ethylene- $\alpha$ -olefin copolymer or a styrene-based block copolymer (Japanese Patent Laid-Open Publication No. Hei 11-130921).

Also, in a technique <3>, a polyethylene resin composition that undergoes crosslinking upon exposure to 15 electron beam has been proposed. This composition is composed of a polyethylene and a highly crosslinkable ethylene copolymer obtained by copolymerization of a non-conjugated diene having 8 or more carbon atoms (Japanese Patent Laid-Open Publication No. Hei 7-48482). In a 20 technique <4>, a molded article has also been proposed that comprises an ethylene interpolymer (preferably, uniformly branched ethylene polymer) copolymerized with at least one other monomers and that is formed by curing, irradiating, or crosslinking the ethylene polymer (National Publication 25 of PCT application No. 2002-515530). In a method <5>, also proposed is a crosslinked composition containing silane-

modified polyolefins and polypropylenes (International Patent Publication No. WO 01/038433).

Furthermore, in a technique <6>, a method for producing a particular elastomer has been proposed. In this 5 method, a composition containing an ethylene-propylene rubber, a crystalline polymer (preferably, polyethylene) and an inorganic filler is exposed to an ionizing radiation to cause the composition to undergo crosslinking and thus form the elastomer (Japanese Patent Laid-Open Publication 10 No. Sho 51-59981). In a technique <7>, a composition has also been proposed that has been improved in its properties such as oil-resistance, cut-through property, thermal deformation, and solder resistance. This composition is obtained by crosslinking a particular crosslinkable resin 15 composition either chemically or by exposure to an electron beam. The crosslinkable resin composition is composed of a styrene-ethylene/butylene-styrene block copolymer, a polypropylene, an oil, a stabilizer, and a crosslinking aid (Japanese Patent Laid-Open Publication No. 58-145751). In a 20 technique <8>, a heat-resistant and flame-resistant crosslinkable polyethylene composition has been proposed that is obtained by causing a particular composition to undergo crosslinking either chemically or by exposure to an electron beam. The composition is composed of a 25 polyethylene, a styrene-ethylene/butylene-styrene block copolymer, and a flame retardant (Japanese Patent Laid-Open

Publication No. Sho 59-105040).

However, the method <1>, which involves addition of a crosslinkable monomer and irradiation with an active energy ray, cannot necessarily provide the resulting crosslinkable 5 polymer composition with sufficient heat resistance or solvent resistance. In the method <2>, in which a polyethylene is mixed with an ethylene- $\alpha$ -olefin copolymer or a styrene-based block copolymer, the addition of ethylene- $\alpha$ -olefin copolymer does not significantly improve 10 the heat resistance of the resulting resin, while the addition of styrene-based block copolymer often results in a reduced solvent resistance of the resin. Thus, the method is not appropriate when it is desired to obtain a 15 composition that exhibits flexibility and heat resistance in a well-balanced manner.

Although each of the techniques <3> through <5> is effective in facilitating crosslinking of the resin, as well as in improving the heat resistance of the resin, none is effective in improving the flexibility of the resin and 20 is thus suitable for applications that require high flexibility.

Involving an ethylene-propylene copolymer rubber or a styrene-ethylene/butylene-styrene block copolymer as an elastic component, the techniques <6> through (8) are each 25 effective to some extent in increasing the flexibility of the resin. However, each of these techniques fails to

impart sufficient crosslinkability and, thus, heat resistance to the resin and is not suitable for use in applications that require high heat resistance, such as wire coatings intended for use in the engine room of

5 automobiles.

For these reasons, a demand exists for a polyolefin-based resin composition that exhibits flexibility, mechanical properties, heat resistance, and solvent resistance in a well-balanced manner and is thus suitable

10 for use in applications such as wire coatings, cable coatings, tubes, films, and sheets.

#### DISCLOSURE OF THE INVENTION

In view of the above-described drawbacks of

15 conventional technologies, it is an object of the present invention to provide a polyolefin-based resin composition that exhibits flexibility, heat resistance, mechanical properties, and solvent resistance in a well-balanced manner.

20 The present invention achieves this object by providing the following compositions, articles and laminates.

(1) A polyolefin-based resin composition, containing an addition polymerization-based block copolymer (I) and a

25 polyolefin-based resin (II), wherein:

the addition polymerization-based block copolymer (I)

is selected from block copolymers comprising at least one polymer block A and at least one polymer block B, and the hydrogenated products thereof;

the polymer block A essentially comprises an aromatic 5 vinyl compound unit containing at least 1% by mass of an alkylstyrene-derived structural unit (a) (which may be referred to simply as "structural unit (a)," hereinafter) in which at least one alkyl group having 1 to 8 carbon atoms is bound to a benzene ring; the polymer block B 10 essentially comprises a conjugated diene compound unit;

at least the moiety of polymer block A can undergo crosslinking upon exposure to an active energy ray; and

after molded into a desired shape, the composition is exposed to an active energy ray to carry out the 15 crosslinking reaction.

(2) The polyolefin-based resin composition according to (1) above, wherein the alkylstyrene-derived structural unit (a) in which at least one alkyl group having 1 to 8 carbon atoms is bound to a benzene ring is a p- 20 methylstyrene unit.

(3) The polyolefin-based resin composition according to (1) or (2) above, wherein the active energy ray is an electron beam.

(4) The polyolefin-based resin composition according 25 to any one of (1) to (3) above, further containing a photopolymerization initiator.

(5) A molded article obtained from the polyolefin-based resin composition according to any one of (1) to (4) above.

(6) A laminate comprising a layer formed of the 5 polyolefin-based resin composition according to any one of (1) to (4) above.

BEST MODE FOR CARRYING OUT THE INVENTION

The present invention will now be described in 10 further detail.

The addition polymerization-based block copolymer (I) for forming the polyolefin-based resin composition of the present invention is selected from block copolymers comprising at least one polymer block A and at least one 15 polymer block B, and the hydrogenated products thereof. The polymer block A essentially comprises an aromatic vinyl compound unit that contains at least 1% by mass of an alkylstyrene-derived structural unit (a) in which at least one alkyl group having 1 to 8 carbon atoms is bound to a 20 benzene ring. The polymer block B essentially comprises a conjugated diene compound unit. At least the moiety of polymer block A can undergo crosslinking upon exposure to an active energy ray.

Examples of alkylstyrenes for forming the structural 25 unit (a) of the polymer block A include o-alkylstyrene, m-alkylstyrene, p-alkylstyrene, 2,4-dialkylstyrene, 3,5-

dialkylstyrene, and 2,4,6-trialkylstyrene with their alkyl groups having 1 to 8 carbon atoms, and halogenated alkylstyrenes in which one or more of the hydrogen atoms borne by the alkyl groups of the alkylstyrenes have been 5 substituted with halogen atoms. Specific examples of the alkylstyrenes for forming the structural unit (a) include o-methylstyrene, m-methylstyrene, p-methylstyrene, 2,4-dimethylstyrene, 3,5-dimethylstyrene, 2,4,6-trimethylstyrene, o-ethylstyrene, m-ethylstyrene, p-10 ethylstyrene, 2,4-diethylstyrene, 3,5-diethylstyrene, 2,4,6-triethylstyrene, o-propylstyrene, m-propylstyrene, p-propylstyrene, 2,4-dipropylstyrene, 3,5-dipropylstyrene, 2,4,6-tripropylstyrene, 2-methyl-4-ethylstyrene, 3-methyl-5-ethylstyrene, o-chloromethylstyrene, m-15 chloromethylstyrene, p-chloromethylstyrene, 2,4-bis(chloromethyl)styrene, 3,5-bis(chloromethyl)styrene, 2,4,6-tri(chloromethyl)styrene, o-dichloromethylstyrene, m-dichloromethylstyrene, and p-dichloromethylstyrene.

The polymer block A may contain one or more units of 20 the above-described alkylstyrenes and halogenated alkylstyrenes for forming the structural unit (a). Of these, p-methylstyrene unit and is particularly preferred as the structural unit (a), because it readily undergoes crosslinking and is readily commercially available.

25 Examples of the aromatic vinyl compound units other than those for forming the structural unit (a) include

those formed of styrene,  $\alpha$ -methylstyrene,  $\beta$ -methylstyrene, monofluorostyrene, difluorostyrene, monochlorostyrene, dichlorostyrene, methoxystyrene, vinylnaphthalene, vinylanthracene, indene, and acetonaphthylene. Of these, 5 styrene and  $\alpha$ -methylstyrene are particularly preferred.

The polymer block A of the addition polymerization-based block copolymer (I) forms hard segments of the thermoplastic elastomer. The alkyl groups, which are each bound to a benzene ring to form the structural unit (a), 10 serve to introduce cross linkages in the hard segments of the polymer block A as they undergo the static crosslinking reaction upon exposure to an active energy ray.

The proportion of the structural unit (a) in the polymer block A is 1% by mass or more and, preferably, 10% 15 by mass or more, and more preferably 40% by mass or more with respect to the mass of the polymer block A that forms the addition polymerization-based block copolymer (I) (or the total mass of the polymer blocks A when the addition polymerization-based copolymer (I) contains two or more 20 polymer blocks A). The polymer block A may be made entirely of the structural unit (a). If the proportion of the structural unit (a) is less than 1% by mass, then the cross linkages are not introduced into the polymer block A to a sufficient degree, resulting in insufficient heat 25 resistance and mechanical properties of the resulting polyolefin-based resin composition. In the polymer block A,

the structural unit (a) and other aromatic vinyl compound units may be linked to one another either randomly, in blocks or in tapered blocks.

Preferably, the polymer block A is present in the 5 addition polymerization-based block copolymer (I) in an amount of 10 to 40% by mass. If the amount of the polymer block A is less than 10% by mass, then insufficient crosslinking results, leading to insufficient heat resistance and mechanical properties. If the amount of the 10 polymer block A is greater than 40% by mass, then the resulting polyolefin-based resin composition does not show sufficient flexibility.

When necessary, the polymer block A may include, along with the structural unit composed of the aromatic 15 vinyl compound containing the structural unit (a), a small amount of structural units composed of other polymerizable monomers. The proportion of the structural unit composed of such other polymerizable monomers is preferably 30% by mass or less and, more preferably, 10% by mass or less based on 20 the mass of the polymer block A that forms the addition polymerization-based block copolymer (I) (or the total mass of the polymer blocks A when the addition polymerization-based copolymer (I) contains two or more polymer blocks A). Examples of the other polymerizable monomers include 1- 25 butene, pentene, hexene, butadiene, isoprene, and methyl vinyl ether.

Aside from the polymer block A composed of the aromatic vinyl compound unit containing the structural unit (a), the addition polymerization-based block copolymer (I) for use in the present invention may contain a polymer 5 block composed of an aromatic vinyl compound that does not contain the structural unit (a).

The polymer block B of the addition polymerization-based copolymer (I) is composed essentially of a conjugated diene compound unit. Examples of the conjugated diene 10 compounds include butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, and 1,3-hexadiene. The polymer block B may be composed solely of one of these conjugated diene compounds, or it may be composed of two or more of the conjugated diene compounds. The polymer block B is 15 preferably composed of butadiene, isoprene, or a mixture of butadiene and isoprene. The polymer block B may have any microscopic structure, which may be present in any amount. When two or more conjugated dienes are used, they may be linked to one another either randomly, in blocks, in 20 tapered blocks, or in combination of two or more of these manners of linking.

When necessary, the polymer block B may contain, along with the structural unit composed of the conjugated diene compound, a small amount of structural units composed 25 of other polymerizable monomers. The proportion of such other polymerizable monomers is preferably 30% by mass or

less and, more preferably, 10% by mass or less based on the mass of the polymer block B that forms the addition polymerization-based block copolymer (I) (or the total mass of the polymer blocks B when the addition polymerization-  
5 based copolymer (I) contains two or more polymer blocks B).

Examples of the other polymerizable monomers include styrene,  $\alpha$ -methylstyrene, and the aforementioned alkylstyrenes for forming the structural unit (a) (preferably, p-methylstyrene).

10 It is particularly preferred that the polymer block B be a polyisoprene block composed of isoprene units or a hydrogenated polyisoprene block in which some or all of the carbon-carbon double bonds originating from the isoprene units have been hydrogenated; a polybutadiene block  
15 composed of butadiene units or a hydrogenated polybutadiene block in which some or all of the carbon-carbon double bonds originating from the butadiene units have been hydrogenated; or a copolymer block composed of isoprene units and butadiene units or a hydrogenated copolymer block  
20 in which some or all of the carbon-carbon double bonds originating from the isoprene units or the butadiene units have been hydrogenated.

As far as the polymer block A and the polymer block B are linked to one another, they may be linked in any manner  
25 of linking, forming a straight-chained, branched or radial molecule of the addition polymerization-based block

copolymer (I). Two or more of these manners of linking may be combined in one molecule. Preferably, the polymer block A and the polymer block B are linked together to form a straight-chained molecule. Examples of the straight-chained molecules include triblock copolymers as denoted by A-B-A, tetrablock copolymers as denoted by A-B-A-B and pentablock copolymers as denoted by A-B-A-B-A, given that "A" represents the polymer block A and "B" represents the polymer block B. Of these, triblock copolymers ("A-B-A") are particularly preferred because of their flexibility and readiness of the production of the addition polymerization-based block copolymer (I).

While the addition polymerization-based copolymer (I) for use in the present invention may have any number 15 average molecular weight, it preferably has a number average molecular weight in the range of 30000 to 1000000, and more preferably in the range of 40000 to 300000. The term "number average molecular weight" as used herein refers to a number average molecular weight as determined 20 by gel permeation chromatography (GPC) using polystyrene standards.

The addition polymerization-based copolymer (I) of the present invention can be produced, for example, by a known anionic polymerization technique. Specifically, the 25 alkylstyrene for forming the structural unit (a), or a mixture of the alkylstyrene for forming the structural unit

(a) and the aromatic vinyl compound, and the conjugated diene compound are sequentially polymerized to form a block copolymer (*i.e.*, non-hydrogenated form of the addition polymerization-based block copolymer (I)). Using an 5 initiator such as an alkylolithium compound, the reaction is carried out in n-hexane, cyclohexane, or other organic solvents that are inert to the polymerization.

When necessary, the resulting block copolymer is hydrogenated. The hydrogenation reaction is generally 10 carried out in a saturated hydrocarbon solvent such as cyclohexane at a reaction temperature of 20 to 100°C under a hydrogen pressure of 0.1 to 10MPa and in the presence of a hydrogenation catalyst, resulting in a hydrogenated product of the addition polymerization-based block copolymer (I). 15 Examples of such hydrogenation catalysts include Raney nickels; heterogeneous catalysts containing metals, such as Pt, Pd, Ru, Rh and Ni, carried by carbon, alumina, diatomite, and other suitable carriers; Ziegler catalysts containing an organic metal compound of, for example, cobalt, nickel and other group 9 or group 10 metals, 20 combined with an organoaluminum compound or organolithium compound, such as triethylaluminum and triisobutylaluminum; and metallocene catalysts containing a bis(cyclopentadienyl) compound of transition metals, such as titanium, zirconium, and hafnium, combined with an 25 organic metal compound, such as lithium, sodium, potassium,

aluminum, zinc, magnesium or the like.

While the degree of hydrogenation may be adjusted depending on what physical properties are required of the polyolefin-based resin composition of the present invention, 5 it is preferred that 70% of more, preferably 85% or more, and more preferably 95% or more of the carbon-carbon double bonds that result from the conjugated diene compound units of the polymer block B for forming the addition polymerization-based block copolymer (I) are hydrogenated 10 when heat resistance, weather resistance, and ozone resistance are considered particularly important.

The degree of hydrogenation of the carbon-carbon double bonds that result from the conjugated diene compound units of the polymer block B can be determined by measuring 15 the amount of the carbon-carbon double bonds in the polymer block B before the hydrogenation reaction and the amount after the hydrogenation reaction by means of iodimetry, IR spectrophotometry, nuclear magnetic resonance or other suitable techniques and taking the difference between these 20 amounts.

Examples of the polyolefin resin (II) for forming the polyolefin-based resin composition of the present invention include homopolymers, such as high density polyethylene (HDPE), middle density polyethylene, low density 25 polyethylene (LDPE), and polypropylene; ethylene- $\alpha$ -olefin copolymers, such as ethylene-propylene copolymer, ethylene-

1-butene copolymer, ethylene-1-hexene copolymer, ethylene-1-heptene copolymer, ethylene-1-octene copolymer, ethylene-4-methyl-1-pentene copolymer, ethylene-1-nonene copolymer, and ethylene-1-decene copolymer; crosslinkable ethylene-based copolymers, such as ethylene-1,7-octadiene copolymer; and ethylene-vinyl acetate copolymers, ethylene-acrylic acid copolymers, ethylene-acrylate copolymers, ethylene-methacrylic acid copolymers and ethylene-methacrylate copolymers, and resins obtained by modifying these 10 copolymers with maleic anhydride or the like. Of these, high density polyethylene, middle density polyethylene, low density polyethylene, polypropylene, ethylene-propylene copolymer, and ethylene- $\alpha$ -olefin copolymer are particularly preferred.

15 Preferably, the polyolefin-based resin composition of the present invention contains the addition polymerization-based copolymer (I) and the polyolefin-based resin (II) at a mass ratio of the addition polymerization-based copolymer (I) to the polyolefin-based resin (II) of 90/10 to 1/99 and, 20 more preferably, 80/20 to 20/80. If the amount of the polyolefin-based resin (II) relative to the total mass of the addition polymerization-based block copolymer (I) and the polyolefin-based resin (II) is 10% by mass or less, or 99% by mass or more, then the resulting polyolefin-based 25 resin composition often does not exhibit flexibility, heat resistance, mechanical properties, and solvent resistance

in a well-balance manner.

In the polyolefin-based resin composition of the present invention, the active energy ray that is used to crosslink at least the moiety of polymer block A of the 5 addition polymerization-based block copolymer (I) may be a particle beam, electromagnetic wave, and combination of these. Examples of the particle beam include electron beam (EB) and  $\alpha$ -ray, and examples of the electromagnetic wave include ultraviolet ray (UV), visible light, infrared ray, 10  $\gamma$ -ray, and X-ray. Of these, electron beam (EB) and ultraviolet ray (UV) are particularly preferred.

These active energy rays can be irradiated using known apparatuses. The electron beam may be accelerated at a voltage of 0.1 to 10MeV and irradiated at a dose of 1 to 15 500kGy. A lamp with an irradiation wavelength of 200 to 450 nm may be preferably used as the source of ultraviolet ray (UV). Examples of the electron beam (EB) source include tungsten filament, and examples of the ultraviolet ray (UV) source include low-pressure mercury-vapor lamp, high-pressure mercury-vapor lamp, ultraviolet mercury lamp, 20 carbon arc lamp, xenon lamp, and zirconium lamp.

When the active energy ray is irradiated to crosslink at least the moiety of polymer block A of the addition polymerization-based block copolymer (I) in the polyolefin-based resin composition of the present invention, it is not only the moiety of polymer block A that is crosslinked, but

the moiety of polymer block B of the addition polymerization-based block copolymer (I) and the polyolefin-based resin (II) could also be partly crosslinked. However, such cross-linkages, if any, do not 5 interfere with the object of the invention.

When necessary, and especially when ultraviolet ray (UV) is used as the active energy beam, a photopolymerization initiator is further added to the polyolefin-based resin composition of the present invention.

10 Examples of such photopolymerization initiators include, but are not limited to, benzophenone, benzoin, benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether,  $\alpha$ -methylolbenzoin,  $\alpha$ -methylolbenzoin methyl ether,  $\alpha$ -methoxybenzoin methyl ether, benzoin phenyl ether, and  $\alpha$ -t-15 butylbenzoin. These photopolymerization initiators may be used either individually or in combination of two or more photopolymerization initiators. While the photopolymerization initiator, when used, may be added to the polyolefin-based resin composition in any amount, it is 20 preferably added in an amount of 0.01 to 5% by mass with respect to the total mass of the addition polymerization-based block copolymer (I) and the polyolefin-based resin (II).

When necessary, a crosslinking aid is further added 25 to the polyolefin-based resin composition of the present invention. Examples of such crosslinking aids include

triallyl isocyanulate, triallyl cyanulate, N,N'-phenylenebismaleimide, ethylene glycol di(meth)acrylate, propanediol di(meth)acrylate, butanediol di(meth)acrylate, hexanediol di(meth)acrylate, nonanediol di(meth)acrylate, 5 and trimethylolpropane tri(meth)acrylate. These crosslinking aids may be used either individually or in combination of two or more crosslinking aids. While the crosslinking aid, when used, may be added to the polyolefin-based resin composition in any amount, it is 10 preferably added in an amount of 0.01 to 5% by mass with respect to the total mass of the addition polymerization-based block copolymer (I) and the polyolefin-based resin (II).

When necessary, a softener is further added to the 15 polyolefin-based resin composition of the present invention. Examples of such softeners include petroleum-based softeners, such as paraffin-, naphthene- or aromatic compound-based processed oils; liquid paraffin; and vegetable oil-based softeners, such as peanut oil and rosin. 20 These softeners may be used either individually or as a mixture of two or more softeners. While the softener, when used, may be added to the polyolefin-based resin composition in any amount that does not interfere with the object of the present invention, it is typically added in 25 an amount of 300 parts by mass or less, preferably 100 parts by mass or less, with respect to 100 parts by mass of

the addition polymerization-based block copolymer (I).

A filler may be further added to the polyolefin-based resin composition of the present invention for the purpose of improving fillability, heat resistance, and rigidity of 5 the composition. Examples of such fillers include talc, glass fiber, mica, kaolin, titanium oxide talc, clay, calcium silicate, glass, hollow glass sphere, calcium carbonate, magnesium carbonate, aluminum hydroxide, magnesium hydroxide, calcium aluminate, calcium hydroxide, 10 zinc borate, dawsonite, poly-ammonium phosphate, hydrotalcites, silica, alumina, titanium oxide, iron oxide, zinc oxide, magnesium oxide, tin oxide, antimony oxide, barium ferrite, strontium ferrite, carbon black, graphite, carbon fiber, activated carbon, hollow carbon sphere, 15 calcium titanate, silicon carbide, wood filler, starch or the like.

As long as the object of the present invention is not affected, various additives may be added to the polyolefin-based resin composition of the present invention, including 20 thermostabilizers, photostabilizers, UV-absorbents, antioxidants, lubricants, coloring agents, antistats, flame retardants, blowing agents, water repellants, waterproof agents, fluorescent agents, anti-blocking agents, metal inactivating agents, antimicrobial agents, or the like.

25 As long as the object of the present invention is not affected, other polymers may be added to the polyolefin-

based resin composition of the present invention for the purpose of improving flexibility and fluidity. Examples of such polymers include natural rubber, synthetic polyisoprene rubber, liquid polyisoprene rubber and 5 hydrogenated products thereof, polybutadiene rubber, liquid polybutadiene rubber and hydrogenated products thereof, styrene-butadiene rubber, chloroprene rubber, ethylene-propylene rubber, acrylic rubber, butyl rubber, acrylonitrile-butadiene rubber, and styrene-based 10 elastomers, such as polystyrene-polyisoprene-polystyrene block copolymer, polystyrene-polybutadiene-polystyrene block copolymer, hydrogenated products thereof or the like 15 uke.

As long as the object of the present invention is not affected, a thermoplastic polyester resin, polyamide resin, polyphenylene ether resin, or other reinforcing resins 20 having a relatively small molecular weight may be added to the polyolefin-based resin composition of the present invention for the purpose of ensuring the balance between the heat resistance, solvent resistance, and other properties of the composition.

Using a common tank-type mixer, high-speed stirrer, enclosed kneader, internal mixer or extruder, such as a single screw extruder and a twin screw extruder, the 25 polyolefin-based resin composition of the present invention can be prepared by melting/mixing together the addition

polymerization-based block copolymer (I), the polyolefin-based resin (II), and the optional photopolymerization initiator, crosslinking auxiliary, softener, and other optional components. The melting/mixing is carried out at 5 130°C to 230°C and, when necessary, in a nitrogen atmosphere. The resulting polyolefin-based resin composition may be formed into different forms depending on its intended applications and the manner of usage: it may be formed into blocks, granules, flakes, pellets, sticks, films, sheets, 10 and other forms suitable for use in wire coatings, coatings of various cables, tubes, films, and sheets.

Upon the melting/mixing, maleic anhydride and a peroxide (such as dicumylperoxide, di-t-butylperoxide, and 2,5-dimethyl-2,5-di(t-butylperoxy)hexane) may further be 15 added. In this manner, one or both of the addition polymerization-based block copolymer (I) and the polyolefin-based resin (II) are modified with maleic anhydride, so that the resulting polyolefin resin composition acquires an ability to disperse the filler 20 and/or an ability to form a multilayer structure with, or adhere to, a polar resin, such as polyamide, polycarbonate, polybutylene terephthalate and polyethylene terephthalate.

The polyolefin-based resin composition obtained in the above-described manner is then molded by various 25 molding techniques, such as injection molding (e.g., insert molding, double molding, sandwich molding, and gas

injection molding), extrusion molding, inflation molding, T-die film molding, laminate molding, blow molding, hollow molding, compression molding, and calendering. Once 5 molded/processed, the composition is irradiated with the active energy ray to form cross-linkages.

The molded/processed articles can be used in wire coatings, films, such as food wrapping film and fiber wrapping film, processed paper, pipes, sheets, stationeries, food containers, daily commodities, and other applications.

10 The so-obtained polyolefin-based resin composition is formed into a layer, which is laminated with a layer of other polyolefin-based resin, such as polypropylene, and when necessary, an adhesive layer or other layers to form a flexible laminate.

15 An adhesive resin may be added to the polyolefin-based resin composition preferably in an amount of 1 to 500 parts by mass to make the composition adhesive. The resin is then molded into, for example, a film to serve as an adhesive film. Examples of such adhesive resins include 20 rosin-based resins, terpene-based resins, aliphatic petroleum resins, aromatic petroleum resins, alicyclic petroleum resins, coumarone and indene resins, styrene-based resins, alkylphenol resins, and xylene resins.

The present invention will now be described in 25 further detail with reference to examples, which are not intended to limit the scope of the invention in any way.

In each of Examples and Comparative Examples described below, an exemplary polyolefin-based resin composition was evaluated for its hardness, mechanical properties (e.g., tensile strength at break and elongation at break), heat resistance, and solvent resistance. The evaluation was made according to the following methods.

5 1) Hardness

The hardness was measured according to the method described in JIS 6253. Specifically, three sheets (15cm long × 15cm wide × 0.2cm thick each) that were made of one of the polyolefin-based resin compositions obtained in Examples and Comparative Examples, were piled on top of one another and the hardness of the pile was measured using an ASTM D hardness meter as an index of the flexibility.

10 15 2) Mechanical properties (e.g., tensile strength at break and elongation at break)

The mechanical properties were measured according to the method described in JIS K 6251. Specifically, two No. 5 dumbbell-shape sample pieces were stamped out of a 15cm long × 15cm wide × 0.1cm thick sheet that were made of one of the polyolefin-based resin compositions obtained in Examples and Comparative Examples and were stretched on an INSTRON universal tester at a rate of 500mm/min, one at 23°C and the other at 80°C, to determine the tensile strength at break (MPa) and the elongation at break (%) for each sample piece.

## 3) Heat resistance

## 3-1) Residual tensile strength at break and residual elongation at break

The residual tensile strength at break and residual elongation at break were measured according to the method described in Item No. 17 of JIS C 3005. Specifically, a 15cm long × 15cm wide × 0.1cm thick sheet made of one of the polyolefin-based resin compositions obtained in Examples and Comparative Examples was left at 120°C for 96 hours. Subsequently, a No. 5 dumbbell-shaped sample piece as specified by JIS K 6251 was stamped out of the sheet and was stretched on an INSTRON universal tester at a rate of 500mm/min at 23°C to determine the tensile strength at break (MPa) and the elongation at break (%). The residual tensile strength at break and the residual elongation at break were then determined by the following equations:

$$\text{Residual tensile strength at break (\%)} = 100 \times F_1/F_0$$

where  $F_0$  = tensile strength at break (MPa) before heating; and  $F_1$  = tensile strength at break (MPa) after heating;

$$\text{Residual elongation at break (\%)} = 100 \times L_1/L_0$$

where  $L_0$  = elongation at break (%) before heating; and  $L_1$  = elongation at break (%) after heating.

## 3-2) Heat deformation

The heat deformation was measured according to the method described in Item No. 23 of JIS C 3005. Specifically, a 3cm long × 1.5cm wide sample piece was stamped out of a 5 15cm long × 15cm wide × 0.2cm thick sheet made of one of the polyolefin-based resin compositions obtained in Examples and Comparative Examples. The sample piece, along with a heat deformation tester, was preheated at 150°C for 30 minutes. The tester included two parallel plates and a 10 35mm long rod (5mm in radius) that had a semicircular cross-section and was arranged between the parallel plates. After the heating period, the sample piece was placed on the rod and was further left at the same temperature for 30 minutes while a 1kg load was applied to the parallel plates. 15 While the load was still applied, the thickness of the sample piece was measured and the heat deformation was determined by the following equation from the thickness of the sample piece after heating and the thickness before heating. A small heat deformation indicates that the 20 composition has a high heat resistance.

$$\text{Heat deformation (\%)} = 100 \times (M_0 - M_1) / M_0$$

where  $M_0$  = thickness (mm) of the sample piece before 25 heating; and  $M_1$  = thickness (mm) of the sample piece after heating.

## 3-3) Deformation temperature

A No. 6 dumbbell-shaped sample piece as specified by JIS K 6251 was stamped out of a 15cm × 15cm × 0.1cm sheet made of one of the polyolefin-based resin compositions 5 obtained in Examples and Comparative Examples. The sample piece was suspended in an oven while a 72g load was applied. The temperature in the oven was then raised at a rate of 3°C/min to the point at which the sample piece was stretched by 100%. This temperature was measured as an index of the 10 heat resistance of the composition.

## 4) Toluene extraction

A portion of the No.5 dumbbell-shaped sample piece used in the measurement of mechanical properties was cut out and was precisely weighed to make a sample piece 15 (approx. 0.3g). The sample piece was placed in 30ml toluene in a 50ml screw tube. The tube was then agitated on an agitator at 25°C for 12 hours. Subsequently, the sample piece was taken out from the tube and was dried at 100°C for 180 minutes under a reduced pressure. The dried sample 20 piece was weighed. The toluene extraction was determined by the following equation from the weight of the dried sample piece. The toluene extraction so obtained serves as an index of the solvent resistance of the composition.

$$25 \quad \text{Toluene extraction (\%)} = 100 \times (A_0 - A_1) / A_0$$

where  $A_0$  = mass (g) of the sample piece before test; and  $A_1$  = mass (g) of the sample piece after test.

Reference Example 1

39kg cyclohexane and a 180ml cyclohexane solution of 5 sec-butyllithium (11% by mass) were placed in a pressure vessel equipped with a stirrer. To this solution, 1.32kg of a mixture of p-methylstyrene and styrene (p-methylstyrene/styrene = 50/50 (by mass)) were added over a 30-minute period and the polymerization was allowed to 10 proceed at 50°C for 60 minutes. Subsequently, 10.7kg of a mixture of isoprene and butadiene (isoprene/butadiene = 50/50 (by mass)) were added over a 60-minute period and the polymerization was allowed to proceed at 50°C for 90 minutes. Additional 1.32kg of the mixture of p-methylstyrene and 15 styrene (p-methylstyrene/styrene = 50/50 (by mass)) were added over a 30-minute period and the polymerization was allowed to proceed at 50°C for 60 minutes. This gave a reaction mixture containing a poly(p-methylstyrene/styrene)-poly(isoprene/butadiene)-poly(p-methylstyrene/styrene) triblock copolymer. The resulting 20 block copolymer had a number average molecular weight of 94000, and the total amount of p-methylstyrene and styrene as determined by  $^1\text{H-NMR}$  was 20% by mass.

To the resulting reaction mixture containing the 25 block copolymer, a hydrogenation catalyst, which was separately prepared by adding 380g of triisopropylaluminum

(20% by mass, cyclohexane solution) to 56g of nickel octanoate (64% by mass, cyclohexane solution), was added, and the hydrogenation reaction was allowed to proceed at 80°C in a hydrogen atmosphere of 1MPa. This gave a 5 hydrogenated product of the poly(p-methylstyrene/styrene)-poly(isoprene/butadiene)-poly(p-methylstyrene/styrene) triblock copolymer (The product is referred to as "block copolymer (I)-1," hereinafter). The resulting block copolymer (I)-1 had a number average molecular weight of 10 100000, and the total amount of p-methylstyrene and styrene and the degree of hydrogenation as determined by <sup>1</sup>H-NMR were 19% by mass and 97%, respectively.

Reference Example 2

39kg cyclohexane and a 265ml cyclohexane solution of 15 sec-butyllithium (11% by mass) were placed in a pressure vessel equipped with a stirrer. To this solution, 2.25 kg of p-methylstyrene were added over a 30-minute period and the polymerization was allowed to proceed at 50°C for 60 minutes. Following the addition of 100ml tetrahydrofuran, 20 10.5kg of butadiene were added over a 60-minute period and the polymerization was allowed to proceed at 50°C for 90 minutes. Additional 2.25kg of p-methylstyrene were added over a 30-minute period and the polymerization was allowed to proceed at 50°C for 60 minutes. This gave a reaction 25 mixture containing a poly p-methylstyrene-polybutadiene-poly p-methylstyrene triblock copolymer. The resulting

block copolymer had a number average molecular weight of 80000, and the amount of p-methylstyrene as determined by <sup>1</sup>H-NMR was 30% by mass.

To the resulting reaction mixture containing the 5 block copolymer, a hydrogenation catalyst, which was separately prepared by adding 380g of triisopropylaluminum (20% by mass, cyclohexane solution) to 56g of nickel octanoate (64% by mass, cyclohexane solution), was added, and the hydrogenation reaction was allowed to proceed at 10 80°C in a hydrogen atmosphere of 1MPa. This gave a hydrogenated product of the poly p-methylstyrene-polybutadiene-poly p-methylstyrene triblock copolymer (The product is referred to as "block copolymer (I)-2," hereinafter). The resulting block copolymer (I)-2 had a 15 number average molecular weight of 81000, and the amount of p-methylstyrene and the degree of hydrogenation as determined by <sup>1</sup>H-NMR were 29% by mass and 97%, respectively.

Reference Example 3

39kg cyclohexane and a 180ml cyclohexane solution of 20 sec-butyllithium (11% by mass) were placed in a pressure vessel equipped with a stirrer. To this solution, 1.32 kg of styrene were added over a 30-minute period and the polymerization was allowed to proceed at 50°C for 30 minutes. Subsequently, 10.7kg of a mixture of isoprene and butadiene 25 (isoprene/butadiene = 50/50 (by mass)) were added over a 60-minute period and the polymerization was allowed to

proceed at 50°C for 90 minutes. Additional 1.32kg of styrene were added over a 30-minute period and the polymerization was allowed to proceed at 50°C for 60 minutes. This gave a reaction mixture containing a polystyrene-  
5 poly(isoprene/butadiene)polystyrene triblock copolymer. The resulting block copolymer had a number average molecular weight of 94000, and the amount of styrene as determined by <sup>1</sup>H-NMR was 20% by mass.

To the resulting reaction mixture containing the  
10 block copolymer, a hydrogenation catalyst, which was separately prepared by adding 380g of triisopropylaluminum (20% by mass, cyclohexane solution) to 56g of nickel octanoate (64% by mass, cyclohexane solution), was added, and the hydrogenation reaction was allowed to proceed at  
15 80°C in a hydrogen atmosphere of 1MPa. This gave a hydrogenated product of the polystyrene-  
poly(isoprene/butadiene)polystyrene triblock copolymer (The product is referred to as "block copolymer 1," hereinafter). The resulting block copolymer 1 had a number average  
20 molecular weight of 100000, and the amount of styrene and the degree of hydrogenation as determined by <sup>1</sup>H-NMR were 19% by mass and 97%, respectively.

Reference Example 4

39kg cyclohexane and a 265ml cyclohexane solution of  
25 sec-butyllithium (11% by mass) were placed in a pressure vessel equipped with a stirrer. To this solution, 2.25 kg

of styrene were added over a 30-minute period and the polymerization was allowed to proceed at 50°C for 30 minutes. Following the addition of 100ml tetrahydrofuran, 10.5kg of butadiene were added over a 60-minute period and the 5 polymerization was allowed to proceed at 50°C for 90 minutes. Additional 2.25kg of styrene were added over a 30-minute period and the polymerization was allowed to proceed at 50°C for 30 minutes. This gave a reaction mixture containing a polystyrene-polybutadiene-polystyrene triblock copolymer.

10 The resulting block copolymer had a number average molecular weight of 80000, and the amount of styrene as determined by <sup>1</sup>H-NMR was 30% by mass.

To the resulting reaction mixture containing the block copolymer, a hydrogenation catalyst, which was 15 separately prepared by adding 380g of triisopropylaluminum (20% by mass, cyclohexane solution) to 56g of nickel octanoate (64% by mass, cyclohexane solution), was added, and the hydrogenation reaction was allowed to proceed at 80°C in a hydrogen atmosphere of 1MPa. This gave a 20 hydrogenated product of the polystyrene-polybutadiene-polystyrene triblock copolymer (The product is referred to as "block copolymer 2," hereinafter). The resulting block copolymer 2 had a number average molecular weight of 81000, and the amount of styrene and the degree of hydrogenation 25 as determined by <sup>1</sup>H-NMR were 29% by mass and 97%, respectively.

Examples 1 through 6

In each of Examples 1 through 6, a polyolefin-based resin composition was obtained by melting and mixing the following components on a twin screw extruder: one of the 5 block copolymer (I)-1 and the block copolymer (I)-2 obtained in Reference Examples 1 and 2, respectively; a polyolefin-based resin [PE1 or PE2 (PE1 = NOVATEC LD EH30 (a low-density polyethylene manufactured by Japan Polychem Corporation, MFR (190°C, 2.16kg load) = 2.0g/10min); PE2 = 10 ULTZEX 1520L (a linear low-density polyethylene manufactured by Mitsui Chemicals Co., Ltd., MFR (190°C, 2.16kg load) = 2.3g/10min))]; and an antioxidant. These components were melted and mixed at 200°C in respective proportions (by mass) shown in Table 1 below to give the 15 polyolefin-based resin compositions of Examples 1 through 6. Each of the resulting polyolefin-based compositions was pressed (press temperature = 200°C, press pressure = 10MPa, press time = 3min) to make two sheets, one sized 15cm × 15cm × 0.1cm and the other sized 15cm × 15cm × 0.2cm. The 20 sheets were then irradiated with an electron beam at an accelerating voltage of 5.0MeV and were irradiated at a dose of 200kGy. The resulting sheets of each of the polyolefin-based resin compositions were evaluated for the different performances in the manner described above. The 25 results are shown in Table 1 below.

Table 1

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6
(I) Addition polymerization-based block copolymer						
(I)-1	20	20	50	50		
(I)-2					20	20
(II) Polyolefin resin						
PE1	80		50	50	80	
PE2		80				80
Irganox 1010*	0.1	0.1	0.1	0.1	0.1	0.1
Electron beam dose (kGy)	200	200	200	200	200	200
Hardness (Type D)	31	33	24	27	32	34
Tensile strength at break (23°C, MPa)	25	32	26	33	23	34
Elongation at break (23°C, %)	530	570	510	540	510	570
Residual tensile strength at break (23°C, %)	104	98	- <sup>1)</sup>	- <sup>1)</sup>	106	96
Residual elongation at break (23°C, %)	107	107	- <sup>1)</sup>	- <sup>1)</sup>	108	102
Tensile strength at break (80°C, MPa)	6.3	13	5.1	6.5	7.9	13
Elongation at break (80°C, %)	480	690	550	620	540	660
Heat deformation (%)	20	38	- <sup>1)</sup>	- <sup>1)</sup>	22	38
Deformation temperature (°C)	238	242	222	238	186	204
Toluene extraction (%)	0	0	0	5	0	0

\* Irganox 1010 (Product Name): Hindered phenol-based antioxidant, Ciba Specialty Chemicals Co., Ltd.

<sup>1)</sup> N/A

5

#### Comparative Examples 1 through 6

The same polyolefin-based resin compositions as those used in Examples 1 through 6 were pressed to make sheets, which were directly subjected to evaluation of the same

10 performances without electron beam irradiation. The results are shown in Table 2 below.

Table 2

	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6
(I) Addition polymerization-based block copolymer						
(I)-1	20	20	50	50		
(I)-2					20	20
(II) Polyolefin resin						
PE1	80		50		80	
PE2		80		50		80
Irganox 1010*	0.1	0.1	0.1	0.1	0.1	0.1
Electron beam dose (kGy)	0	0	0	0	0	0
Hardness (Type D)	32	34	21	28	33	35
Tensile strength at break (23°C, MPa)	16	31	32	33	20	36
Elongation at break (23°C, %)	570	590	540	500	590	640
Tensile strength at break (80°C, MPa)	2.9	8.3	2.1	3.3	3.3	9.8
Elongation at break (80°C, %)	240	800	200	590	420	890
Deformation temperature (°C)	94	100	92	96	95	101
Toluene extraction (%)	16	14	34	31	14	13

\* Irganox 1010 (Product Name): Hindered phenol-based antioxidant, Ciba Specialty Chemicals Co., Ltd.)

5 Comparative Examples 7 through 12

In Comparative Examples 7 through 12, sheets were prepared from respective polyolefin-based resin compositions in the same manner as in Examples 1 through 6. The polyolefin-based resin compositions of Comparative Examples 7 through 12 are the same as those used in Examples 1 through 6, respectively, except that the block copolymer (I)-1 and the block copolymer (I)-2 obtained in Reference Examples 1 and 2 were replaced by the block copolymer 1 and the block copolymer 2 obtained in Reference Examples 3 and 4, respectively. The resulting sheets were evaluated for the same performances as described above. The results are shown in Tables 3 and 4 below.

Table 3

	Comp. Ex.7	Comp. Ex.8	Comp. Ex.9	Comp. Ex.10
(I) Addition polymerization-based block copolymer				
1	20	20	50	50
2				
(II) Polyolefin resin				
PE1	80		50	
PE2		80		50
Irganox 1010*	0.1	0.1	0.1	0.1
Electron beam dose (kGy)	200	200	200	200
Hardness (Type D)	31	34	26	26
Tensile strength at break (23°C, MPa)	23	29	28	32
Elongation at break (23°C, %)	550	570	580	580
Residual tensile strength at break (23°C, %)	89	84	- <sup>1)</sup>	- <sup>1)</sup>
Residual elongation at break (23°C, %)	103	97	- <sup>1)</sup>	- <sup>1)</sup>
Tensile strength at break (80°C, MPa)	6.3	11	4.3	5.8
Elongation at break (80°C, %)	550	690	560	630
Heat deformation (%)	34	50	- <sup>1)</sup>	- <sup>1)</sup>
Deformation temperature (°C)	128	220	136	192
Toluene extraction (%)	0	0	7	7

\* Irganox 1010 (Product Name): Hindered phenol-based antioxidant, Ciba Specialty Chemicals Co., Ltd.

<sup>1)</sup> N/A

5

#### Comparative Examples 13 and 14

In Comparative Examples 13 and 14, sheets were prepared from respective polyolefin-based resin compositions in the same manner as in Examples 1 through 6.

10 The polyolefin-based resin compositions of Comparative Examples 13 and 14 were each composed only of one of the polyolefin-based resins (i.e., PE1 or PE2) and an antioxidant and did not contain any of the block copolymers obtained in Reference Examples 1 through 4. The resulting 15 sheets were evaluated for the same performances as described above. The results are shown in Table 4 below.

Table 4

	Comp. Ex. 11	Comp. Ex. 12	Comp. Ex. 13	Comp. Ex. 14
(I) Addition polymerization-based block copolymer				
1				
2	20	20		
(II) Polyolefin resin				
PE1	80		100	
PE2		80		100
Irganox 1010*	0.1	0.1	0.1	0.1
Electron beam dose (kGy)	200	200	200	200
Hardness (Type D)	34	38	38	44
Tensile strength at break (23°C, MPa)	24	34	22	38
Elongation at break (23°C, %)	520	580	560	630
Residual tensile strength at break (23°C, %)	94	96	failed	73
Residual elongation at break (23°C, %)	108	103	failed	89
Tensile strength at break (80°C, MPa)	7.8	12	12	18
Elongation at break (80°C, %)	560	680	600	660
Heat deformation (%)	42	54	18	46
Deformation temperature (°C)	106	206	105	208
Toluene extraction (%)	0	0	0	0

\* Irganox 1010 (Product Name): Hindered phenol-based antioxidant, Ciba Specialty Chemicals Co., Ltd.

5 The results of Tables 1 and 2 indicate that the molded articles formed of the polyolefin-based resin compositions of Examples 1 through 6, which were each irradiated with the active energy ray and were crosslinked, exhibit superior mechanical properties, higher heat 10 resistance, and higher solvent resistance as compared to the corresponding non-irradiated molded articles of Comparative Examples 1 through 6.

The results of Tables 1, 3 and 4 indicate that the molded articles formed of the respective polyolefin-based 15 resin compositions of Examples 1 through 6 are more

favorable, especially in terms of their heat resistance and solvent resistance, than the corresponding molded articles of the respective polyolefin-based resin compositions of Comparative Examples 7 through 12, each of which includes a 5 block copolymer having its hard segment formed of blocks composed solely of styrene units. The molded articles formed of the respective polyolefin-based resin compositions of Examples 1 through 6 are more favorable than the corresponding molded articles formed of the 10 respective polyolefin-based resins of Comparative Examples 13 and 14 especially in terms of their flexibility and heat resistance.

#### INDUSTRIAL APPLICABILITY

15 As set forth, the present invention provides a polyolefin-based resin composition that exhibits flexibility, heat resistance, mechanical properties, and solvent resistance in a well-balanced manner. Having such an advantageous feature, the polyolefin-based resin 20 composition of the present invention can find effective application in a wide variety of products, including wire coatings, coatings of various cables, tubes, films, such as food-wrapping films and fiber-wrapping films, processed paper, pipes, sheets, stationeries, food containers, and 25 daily commodities.